

MASS - TRANSFER OPERATIONS

Third Edition

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MASS-TRANSFER OPERATIONS

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CHAPTER
THIRTEEN

LEACHING

Leaching is the preferential solution of one or more constituents of a solid mixture by contact with a liquid solvent. This unit operation, one of the oldest in the chemical industries, has been given many names, depending to some extent upon the technique used for carrying it out. *Leaching* originally referred to percolation of the liquid through a fixed bed of the solid, but is now used to describe the operation generally, by whatever means it may be done. *Lixiviation* is used less frequently as a synonym for leaching, although originally it referred specifically to the leaching of alkali from wood ashes. The term *extraction* is also widely used to describe this operation in particular, although it is applied to all the separation operations as well, whether mass-transfer or mechanical methods are involved. *Decoction* refers specifically to the use of the solvent at its boiling temperature. When the soluble material is largely on the surface of an insoluble solid and is merely washed off by the solvent, the operation is sometimes called *elutriation* or *elution*. This chapter will also consider these washing operations, since they are frequently intimately associated with leaching.

The metallurgical industries are perhaps the largest users of the leaching operation. Most useful minerals occur in mixtures with large proportions of undesirable constituents, and leaching of the valuable material is a separation method which is frequently applied. For example, copper minerals are preferentially dissolved from certain of their ores by leaching with sulfuric acid or ammoniacal solutions, and gold is separated from its ores with the aid of sodium cyanide solutions. Leaching similarly plays an important part in the metallurgical processing of aluminum, cobalt, manganese, nickel, and zinc. Many naturally occurring organic products are separated from their original structure by leaching. For example, sugar is leached from sugar beets with hot water, vegetable oils are recovered from seeds such as soybeans and cottonseed by

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leaching with organic solvents, tannin is dissolved out of various tree barks by leaching with water, and many pharmaceutical products are similarly recovered from plant roots and leaves. Tea and coffee are prepared both domestically and industrially by leaching operations. In addition, chemical precipitates are frequently washed of their adhering mother liquors by techniques and in equipment quite similar to those used in true leaching operations, as in the washing of caustic soda liquor from precipitated calcium carbonate following the reaction between soda ash and lime.

Preparation of the Solid

The success of a leaching and the technique to be used will very frequently depend upon any prior treatment which may be given the solid.

In some instances, small particles of the soluble material are completely surrounded by a matrix of insoluble matter. The solvent must then diffuse into the mass, and the resulting solution must diffuse out, before a separation can result. This is the situation with many metallurgical materials. Crushing and grinding of such solids will greatly accelerate the leaching action, since then the soluble portions are made more accessible to the solvent. A certain copper ore, for example, can be leached effectively by sulfuric acid solutions within 4 to 8 h if ground to pass through a 60-mesh screen, in 5 days if crushed to 6-mm granules, and only in 4 to 6 years if 150-mm lumps are used [43]. Since grinding is expensive, the quality of the ore will have much to do with the choice of size to be leached. For certain gold ores, on the other hand, the tiny metallic particles are scattered throughout a matrix of quartzite which is so impervious to the leaching solvent that it is essential to grind the rock to pass through a 100-mesh screen if leaching is to occur at all. When the soluble substance is more or less uniformly distributed throughout the solid or even in solid solution, the leaching action may provide channels for the passage of fresh solvent and fine grinding may not be necessary. Collapse of the insoluble skeleton which remains after solute removal may present problems, however.

Vegetable and animal bodies are cellular in structure, and the natural products to be leached from these materials are usually found inside the cells. If the cell walls remain intact upon exposure to a suitable solvent, the leaching action involves osmotic passage of the solute through the cell walls. This may be slow, but it is impractical and sometimes undesirable to grind the material small enough to release the contents of individual cells. Thus, sugar beets are cut into thin, wedge-shaped slices called *cassettes* before leaching in order to reduce the time required for the solvent water to reach the individual plant cells. The cells are deliberately left intact, however, so that the sugar will pass through the semipermeable cell walls while the undesirable colloidal and albuminous materials largely remain behind. For many pharmaceutical products recovered from plant roots, stems, and leaves, the plant material is frequently dried before treatment, and this does much toward rupturing the cell walls and releasing the solute for direct action by the solvent. Vegetable seeds and beans, such as soybeans, are usually rolled or flaked to give particles in the size range 0.15 to

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LEACHING 719

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0.5 mm. The cells are, of course, smaller than this, but they are largely ruptured by the flaking process, and the oils are then more readily contacted by the solvent.

When the solute is adsorbed upon the surface of solid particles or merely dissolved in adhering solution, no grinding or crushing is necessary and the particles can be washed directly.

Temperature of Leaching

It is usually desirable to leach at as high a temperature as possible. Since higher temperatures result in higher solubility of the solute in the solvent, higher ultimate concentrations in the leach liquor are possible. The viscosity of the liquid is lower and the diffusivities larger at higher temperatures, leading to increased rates of leaching. With some natural products such as sugar beets, however, temperatures which are too high may lead to leaching of excessive amounts of undesirable solutes or chemical deterioration of the solid.

Methods of Operation and Equipment

Leaching operations are carried out under batch and semibatch (unsteady-state) as well as under completely continuous (steady-state) conditions. In each category, both stagewise and continuous-contact types of equipment are to be found. Two major handling techniques are used: spraying or trickling the liquid over the solid, and immersing the solid completely in the liquid. The choice of equipment to be used in any case depends greatly upon the physical form of the solids and the difficulties and cost of handling them. This has led in many instances to the use of very specialized types of equipment in certain industries.

UNSTEADY-STATE OPERATION

The unsteady-state operations include those where the solids and liquids are contacted in purely batchwise fashion and also those where a batch of the solid is contacted with a continually flowing stream of the liquid (semibatch method). Coarse solid particles are usually treated in fixed beds by percolation methods, whereas finely divided solids, which can be kept in suspension more readily, can be dispersed throughout the liquid with the help of some sort of agitator.

In-Place (in Situ) Leaching

This operation, also called *solution mining*, refers to the percolation leaching of minerals in place at the mine, by circulation of the solvent over and through the ore body. It is used regularly in the removal of salt from deposits below the earth's surface by solution of the salt in water which is pumped down to the deposit. It has been applied to the leaching of low-grade copper ores containing as little as 0.2 percent copper [34] and to ores as deep as 335 m (1100 ft) below

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CHAPTER
TEN

LIQUID EXTRACTION

Liquid extraction, sometimes called solvent extraction, is the separation of the constituents of a liquid solution by contact with another insoluble liquid. If the substances constituting the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result, and this can be enhanced by use of multiple contacts or their equivalent in the manner of gas absorption and distillation.

A simple example will indicate the scope of the operation and some of its characteristics. If a solution of acetic acid in water is agitated with a liquid such as ethyl acetate, some of the acid but relatively little water will enter the ester phase. Since at equilibrium the densities of the aqueous and ester layers are different, they will settle when agitation stops and can be decanted from each other. Since now the ratio of acid to water in the ester layer is different from that in the original solution and also different from that in the residual water solution, a certain degree of separation will have occurred. This is an example of stagewise contact, and it can be carried out either in batch or in continuous fashion. The residual water can be repeatedly extracted with more ester to reduce the acid content still further, or we can arrange a countercurrent cascade of stages. Another possibility is to use some sort of countercurrent continuous-contact device, where discrete stages are not involved. The use of reflux, as in distillation, may enhance the ultimate separation still further.

In all such operations, the solution which is to be extracted is called the *feed*, and the liquid with which the feed is contacted is the *solvent*. The solvent-rich product of the operation is called the *extract*, and the residual liquid from which solute has been removed is the *raffinate*.

More complicated processes may use two solvents to separate the components of a feed. For example, a mixture of *p*- and *o*-nitrobenzoic acids can be

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